

## PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-265989

(43)Date of publication of application : 07.10.1997

(51)Int.Cl.

H01M 4/60

H01M 4/02

H01M 10/40

(21)Application number : 08-072566

(71)Applicant : YAZAKI CORP

(22)Date of filing : 27.03.1996

(72)Inventor : NAOI KATSUHIKO  
TORIGOE AKIHIKO  
IIZUKA HIROSHI

## (54) ELECTRODE MATERIAL AND SECONDARY BATTERY

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a sulfide family electrode material and a secondary battery, capable of high rate charging/discharging at room temperature by containing a thioketone group in the sulfide family electrode material.

SOLUTION: An organic electrode material is a sulfide family electrode material having a thioketone group. The sulfide family electrode material is a material having sulfur participating in the reaction forming S-S bonding by electrolytic reduction and/or cleaving S-S bonding by electrolytic reduction. As an electron conductive material, carbon or metal powder such as titanium and nickel is use, and as an ion conductive material, a liquid electrolyte prepared by mixing an electrolyte salt such as perchlorate to a solvent such as propylene carbonate and ethylene carbonate, or a solid electrolyte such as polyethylene oxide in which the electrolyte salt is dissolved is listed.

## \* NOTICES \*

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

---

CLAIMS

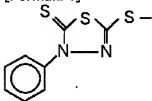
---

[Claim(s)]

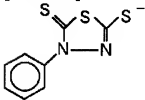
[Claim 1]A sulfide system electrode material having a thioketone group.

[Claim 2]The sulfide system electrode material according to claim 1 having the ion shown in a basis shown in \*\* 1, or/and \*\* 2.

[Formula 1]



[Formula 2]



[Claim 3]The sulfide system electrode material containing a 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one) according to claim 1.

[Claim 4]A rechargeable battery containing a substance which has a thioketone.

[Claim 5]The rechargeable battery containing a compound which has the ion shown in a basis shown in \*\* 1, or/and \*\* 2 according to claim 4.

[Claim 6]The rechargeable battery containing a 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one) according to claim 5.

---

[Translation done.]

\* NOTICES \*

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

## DETAILED DESCRIPTION

---

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the electrode material for cells. It is related with a sulfide system electrode material in detail.

[0002]

[Description of the Prior Art]In recent years, portability-ization of communication equipment or OA equipment progresses and the weight saving of these apparatus and miniaturization competition are developed. The well head-ization is called for also in such various equipment or the rechargeable battery used as a power supply of an electromobile etc. Although the cell using a new electrode material is being developed to this demand, since the energy density is comparatively high in this, the electrode materials (henceforth "a disulfide electrode material") (US,4833048,B etc.) using a disulfide compound attract attention. This thing has a triazine ring or uses for an electrode material the sulfide compound etc. which have a thiadiazole ring.

[0003]here -- a disulfide compound -- R-S-S-R (R is an organic functional group) -- a table -- the bottom at the time. A disulfide bond (SS linkage) cleaves by supply of two electrons by electrolytic reduction, it combines with the cation in an electrolysis solution, or a proton ( $M^+$ ), and it is set to 2 ( $R-S^- - M^+$ ), returns to original R-S-S-R at the time of electrolytic oxidation, and emits two electrons. In this rechargeable battery, it is supposed that the energy density of 150 or more Wh/kg of other usual rechargeable battery averages is expectable. However, from the contents which the artificers of the above-mentioned United States patent have reported by J.Electrochem.Soc.Vol.136.No.9 and p.2570-2575 (1989). The electron transferring rate of the electrode reaction of this sulfide system rechargeable battery was very slow, therefore the problem referred to as that it is difficult to take out the high current corresponding to practical use, and it is restricted to use at not less than 60 \*\* was pointed out near the room temperature.

[0004]Then, this disulfide system rechargeable battery was improved, and as art of making it corresponding to a high current, as shown in JP,H5-74459,A etc., the electrode material which combined conductive polymers, such as poly aniline, with the organic compound which has a thiadiazole ring and a disulfide group was proposed. However, in spite of having performed such improvement, sufficient high current was not able to be too taken out under the room temperature.

[0005]

[Problem(s) to be Solved by the Invention]An object of this invention is to provide the sulfide system electrode material which can take out a room temperature or a high current, and the rechargeable battery which can take out a high current also at a room temperature, when it applies to the electrode material of a rechargeable battery.

[0006]

[Means for Solving the Problem]An organic electrode material of this invention is a sulfide system electrode material as for which the passage according to claim 1 has a thioketone group, in order to

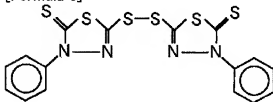
solve the above-mentioned problem.

[0007]

[Embodiment of the Invention] In this invention, a sulfide system electrode material refers to what has a sulfur atom which forms an SS linkage by electrolytic reduction, or participates in/and the reaction for which an SS linkage cleaves by electrolytic reduction. Even if an SS linkage is a disulfide bond formed with two sulfur atoms, it may be what is called polysulfide combination that three or more sulfur atoms shown by S-S-S etc. combined continuously here.

[0008] In the case of the substance which has a basis shown in \*\* 1, or the ion shown in \*\* 2, since the facilitatory effect [ as opposed to generation and the dissociative reaction of an SS linkage by the influence of a phenyl group ] is remarkable, it is desirable. Since there is very little reduction of the capacity also when a charging and discharging cycle increases especially that it is a 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one) (refer to \*\* 3) which is a dimer, it is desirable.

[Formula 3]



[0009] However, in the ion shown in the basis shown in \*\* 1, and \*\* 2, influence of as opposed to generation and the dissociative reaction of an SS linkage in the substituent of the 3rd place is great, therefore these things [ that it is a phenyl group like ] are desirable. However, what introduced an alkyl group, an amino group, a carboxyl group, an alkylamino group, an amide group, or hydrogen, such as an ethyl group, can be used instead of a phenyl group. When it is what has a thiol group instead of a phenyl group, disulfide polymer of thiadiazole thione is formed. The nitrogen atom of the 3rd place in \*\* 1 may be replaced by a carbon atom and others.

[0010] Since the above-mentioned active material does not have conductivity, it mixes with an electronic conducting material and an ion conductive material, and it produces an anode. As an electronic electrical conducting material, metal powders, such as carbon or titanium, and nickel, etc. can be used. As an ion conductive material, electrolyte salt and propylene carbonate, such as a perchlorate, Ethylene carbonate, 1,2-dimethoxyethane, 1,2-diethoxyethane, Gamma-butyrolactone, a tetrahydrofuran, 2-methyltetrahydrofuran, Solid electrolytes, such as polyethylene oxide in which a liquid electrolyte which mixed solvents, such as 1,3-dioxolane, 4-methyl-1,3-dioxolane, diethylether, sulfolane, acetonitrile, propionitrile, and an anisole, or electrolyte salt was dissolved, are mentioned. Although both such a liquid electrolyte and a solid polymer electrolyte can be used as an electrolyte of a cell, when a solid electrolyte is used, since a role of a separator which prevents contact with an anode and a negative electrode is also played simultaneously, it is desirable.

[0011] In the case of a lithium secondary battery, as an electrolyte, it is usable in  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ , etc., for example. It dissolves in the above-mentioned organic solvent, and these form an electrolysis solution so that it may become suitable concentration. As the negative pole, an electrode usually used for a rechargeable battery can be used. For example, in the case of a lithium secondary battery, an intercalation compound with metal lithium, a lithium aluminum alloy or lithium, black lead, carbon, etc., etc. are mentioned. Although a cell is formed combining these anodes, an electrolysis solution, and the negative pole, it is possible to apply regardless of cell shape at that time, i.e., a flat type, cylindrical, or a square shape.

[0012]

[Example]

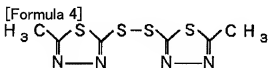
[Composition of a 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one)] Under argon atmosphere, iodine of 5mmol is dissolved in 30 ml of methanol. The solution which dissolved potassium salt (it

receives from HIDORASU chemicals) 10mmol of 5-mercapto-3-phenyl-1,3,4-thiadiazole 2-one in 30 ml of methanol beforehand is slowly dropped at this.

Then, methanol washes the postprecipitation neutralized precipitate which stirred for 3 hours, cooled subsequently to -40 \*\*, and separated the produced sediment by filtration, Ethanol performed recrystallization for this 3 times after reduced pressure drying, and the 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one) (refer to \*\* 3) was obtained.

[0013][Composition of a 2,2'-dithioscrew (5-methyl-1,3,4-thiadiazole)] The solution which dissolved iodine of 5mmol in 30 ml of methanol, and dissolved 2-mercapto-5-methyl-1,3,4-thiadiazole 10mmol and sodium-methoxide 5mmol in 30 ml of methanol beforehand under argon atmosphere at this is dropped slowly.

Then, it stirred for 3 hours, subsequently to -60 \*\* it cooled, and filtration separated the produced sediment, after reduced pressure drying, by ethanol, recrystallization was performed 3 times and the 2,2'-dithioscrew (5-methyl-1,3,4-thiadiazole) (refer to \*\* 4) was obtained.



[0014]About these profitable \*\*\*\* output, it is checked by FAB mass spectrograph and an infrared-spectroscopic-analysis device that it is an object.

[0015]The cell was formed using the 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one) obtained as mentioned above and the 2,2'-dithioscrew (5-methyl-1,3,4-thiadiazole). All the following work was done under the argon air current in a glove box.

[0016]Two electrolysis solutions which dissolved lithium trifluoromethanesulfonate ( $\text{LiCF}_3\text{SO}_3$ ) in 30 ml of gamma-butyrolactone as an electrolyte so that it might become the concentration of 0.2mmol/ l are prepared, Two disulfide compounds, the 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one) compounded above to each of these and a 2,2'-dithioscrew (5-methyl-1,3,4-thiadiazole), were dissolved so that it might become the concentration of 5mmol/ l.

[0017]Using two sorts of these solutions, respectively used glassy carbon as a sample pole, the platinum wire was used as a counter electrode, silver/silver silver chloride electrode was used as a reference pole, and the cell was formed. The cell which has the cell A (EXAMPLE) and a 2,2'-dithioscrew (5-methyl-1,3,4-thiadiazole) for the cell which has a 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one) at this time was used as the cell B (comparative example). In 23 \*\*, the scan speed was made into a second in 50mV /about these cells A and B, and the cyclic voltamogram was measured. Both these results are shown in drawing 1.

[0018]When the cyclic voltamogram of these cells A and the cell B is compared, a gap of the reduction potential which shows the peak of the oxidation potential which shows the peak of oxidation current, and reduction current is 340 mV by the cell A, it is 520 mV by the cell B, and the gap in the cell A is smaller than the gap in the cell B. Therefore, the cell A which has a 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one) concerning this invention according to the electrode reaction theory. Compared with the cell B which has a 2,2'-dithioscrew (5-methyl-1,3,4-thiadiazole) used conventionally, it turns out that it is suitable for the charge and discharge in the high current in a room temperature.

[0019]

[Effect of the Invention]The rechargeable battery produced using the electrode material concerning this invention can take out a high current also at a room temperature as compared with the rechargeable battery using the sulfide system electrode material which has the conventional thiadiazole ring.

---

[Translation done.]

\* NOTICES \*

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

---

TECHNICAL FIELD

---

[Field of the Invention]This invention relates to the electrode material for cells. It is related with a sulfide system electrode material in detail.

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

---

PRIOR ART

[Description of the Prior Art]In recent years, portability-ization of communication equipment or OA equipment progresses and the weight saving of these apparatus and miniaturization competition are developed. The well head-ization is called for also in such various equipment or the rechargeable battery used as a power supply of an electromobile etc. Although the cell using a new electrode material is being developed to this demand, since the energy density is comparatively high in this, the electrode materials (henceforth "a disulfide electrode material") (US,4833048,B etc.) using a disulfide compound attract attention. This thing has a triazine ring or uses for an electrode material the sulfide compound etc. which have a thiadiazole ring.

[0003]here -- a disulfide compound -- R-S-S-R (R is an organic functional group) -- a table -- the bottom at the time. A disulfide bond (SS linkage) cleaves by supply of two electrons by electrolytic reduction, it combines with the cation in an electrolysis solution, or a proton ( $M^+$ ), and it is set to 2 ( $R-S^- - M^+$ ), returns to original R-S-S-R at the time of electrolytic oxidation, and emits two electrons. In this rechargeable battery, it is supposed that the energy density of 150 or more Wh/kg of other usual rechargeable battery averages is expectable. However, from the contents which the artificers of the above-mentioned United States patent have reported by J.Electrochem.Soc.Vol.136.No.9 and p.2570-2575 (1989). The electron transferring rate of the electrode reaction of this sulfide system rechargeable battery was very slow, therefore the problem referred to as that it is difficult to take out the high current corresponding to practical use, and it is restricted to use at not less than 60 °C was pointed out near the room temperature.

[0004]Then, this disulfide system rechargeable battery was improved, and as art of making it corresponding to a high current, as shown in JP,H5-74459,A etc., the electrode material which combined conductive polymers, such as poly aniline, with the organic compound which has a thiadiazole ring and a disulfide group was proposed. However, in spite of having performed such improvement, sufficient high current was not able to be too taken out under the room temperature.

---

[Translation done.]



\* NOTICES \*

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

---

EFFECT OF THE INVENTION

---

[Effect of the Invention]The rechargeable battery produced using the electrode material concerning this invention can take out a high current also at a room temperature as compared with the rechargeable battery using the sulfide system electrode material which has the conventional thiadiazole ring.

---

[Translation done.]

\* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

TECHNICAL PROBLEM

---

[Problem(s) to be Solved by the Invention]An object of this invention is to provide the sulfide system electrode material which can take out a room temperature or a high current, and the rechargeable battery which can take out a high current also at a room temperature, when it applies to the electrode material of a rechargeable battery.

---

[Translation done.]

## \* NOTICES \*

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

## MEANS

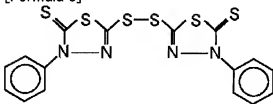
[Means for Solving the Problem]An organic electrode material of this invention is a sulfide system electrode material as for which the passage according to claim 1 has a thioketone group, in order to solve the above-mentioned problem.

[0007]

[Embodiment of the Invention]In this invention, a sulfide system electrode material refers to what has a sulfur atom which forms an SS linkage by electrolytic reduction, or participates in/and the reaction for which an SS linkage cleaves by electrolytic reduction. Even if an SS linkage is a disulfide bond formed with two sulfur atoms, it may be what is called polysulfide combination that three or more sulfur atoms shown by S-S-S etc. combined continuously here.

[0008]In the case of the substance which has a basis shown in \*\* 1, or the ion shown in \*\* 2, since the facilitatory effect [ as opposed to generation and the dissociative reaction of an SS linkage by the influence of a phenyl group ] is remarkable, it is desirable. Since there is very little reduction of the capacity also when a charging and discharging cycle increases especially that it is a 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one) (refer to \*\* 3) which is a dimer, it is desirable.

[Formula 3]



[0009]However, in ion shown in a basis shown in \*\* 1, and \*\* 2, influence of as opposed to generation and dissociative reaction of an SS linkage in a substituent of the 3rd place is great, therefore these things [ that it is a phenyl group like ] are desirable. However, what introduced an alkyl group, an amino group, a carboxyl group, an alkylamino group, an amide group, or hydrogen, such as an ethyl group, can be used instead of a phenyl group. When it is what has a thiol group instead of a phenyl group, disulfide polymer of thiadiazole thione is formed. A nitrogen atom of the 3rd place in \*\* 1 may be replaced by a carbon atom and others.

[0010]Since the above-mentioned active material does not have conductivity, it mixes with an electronic conducting material and an ion conductive material, and it produces an anode. As an electronic electrical conducting material, metal powders, such as carbon or titanium, and nickel, etc. can be used, As an ion conductive material, electrolyte salt and propylene carbonate, such as a perchlorate, Ethylene carbonate, 1,2-dimethoxyethane, 1,2-diethoxyethane, Gamma-butyrolactone, a tetrahydrofuran, 2-methyltetrahydrofuran, Solid electrolytes, such as polyethylene oxide in which a liquid electrolyte which mixed solvents, such as 1,3-dioxolane, 4-methyl-1,3-dioxolane, diethylether, sulfolane, acetonitrile, propionitrile, and an anisole, or electrolyte salt was dissolved, are mentioned.

Although both such a liquid electrolyte and a solid polymer electrolyte can be used as an electrolyte of a cell, when a solid electrolyte is used, since a role of a separator which prevents contact with an anode and a negative electrode is also played simultaneously, it is desirable.

[0011] In the case of a lithium secondary battery, as an electrolyte, it is usable in  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiCF}_3\text{SO}_3$ , etc., for example. It dissolves in the above-mentioned organic solvent, and these form an electrolysis solution so that it may become suitable concentration. As the negative pole, an electrode usually used for a rechargeable battery can be used. For example, in the case of a lithium secondary battery, an intercalation compound with metal lithium, a lithium aluminum alloy or lithium, black lead, carbon, etc., etc. are mentioned. Although a cell is formed combining these anodes, an electrolysis solution, and the negative pole, it is possible to apply regardless of cell shape at that time, i.e., a flat type, cylindrical, or a square shape.

---

[Translation done.]

## \* NOTICES \*

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

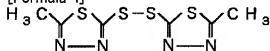
## EXAMPLE

## [Example]

[Composition of a 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one)] Under argon atmosphere, iodine of 5mmol is dissolved in 30 ml of methanol, The solution which dissolved potassium salt (it receives from HIDORASU chemicals) 10mmol of 5-mercapto-3-phenyl-1,3,4-thiadiazole 2-one in 30 ml of methanol beforehand is slowly dropped at this. Then, methanol washes the postprecipitation neutralized precipitate which stirred for 3 hours, cooled subsequently to -40 \*\*, and separated the produced sediment by filtration, Ethanol performed recrystallization for this 3 times after reduced pressure drying, and the 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one) (refer to \*\* 3) was obtained.

[0013][Composition of a 2,2'-dithioscrew (5-methyl-1,3,4-thiadiazole)] The solution which dissolved iodine of 5mmol in 30 ml of methanol, and dissolved 2-mercapto-5-methyl-1,3,4-thiadiazole 10mmol and sodium-methoxide 5mmol in 30 ml of methanol beforehand under argon atmosphere at this is dropped slowly. Then, it stirred for 3 hours, subsequently to -60 \*\* it cooled, and filtration separated the produced sediment, after reduced pressure drying, by ethanol, recrystallization was performed 3 times and the 2,2'-dithioscrew (5-methyl-1,3,4-thiadiazole) (refer to \*\* 4) was obtained.

## [Formula 4]



[0014]About these profitable \*\*\* output, it is checked by FAB mass spectrograph and an infrared-spectroscopic-analysis device that it is an object.

[0015]The cell was formed using the 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one) obtained as mentioned above and the 2,2'-dithioscrew (5-methyl-1,3,4-thiadiazole). All the following work was done under the argon air current in a glove box.

[0016]Two electrolysis solutions which dissolved lithium trifluoromethanesulfonate ( $\text{LiCF}_3\text{SO}_3$ ) in 30 ml of gamma-butyrolactone as an electrolyte so that it might become the concentration of 0.2mmol/l are prepared. Two disulfide compounds, the 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one) compounded above to each of these and a 2,2'-dithioscrew (5-methyl-1,3,4-thiadiazole), were dissolved so that it might become the concentration of 5mmol/l.

[0017]Using two sorts of these solutions, respectively used glassy carbon as a sample pole, the platinum wire was used as a counter electrode, silver/silver silver chloride electrode was used as a reference pole, and the cell was formed. It is the cell A about the cell which has a 5,5'-dithioscrew (3-phenyl-1,3,4-thiadiazole 2-one) at this time.

[Translation done.]

\* NOTICES \*

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.\*\*\* shows the word which can not be translated.

3.In the drawings, any words are not translated.

---

DESCRIPTION OF DRAWINGS

---

[Brief Description of the Drawings]

[Drawing 1]It is a cyclic voltamogram of the cell B which is the cell A and comparative example which are working example of this invention.

---

[Translation done.]

\* NOTICES \*

JP0 and INPIT are not responsible for any damages caused by the use of this translation.

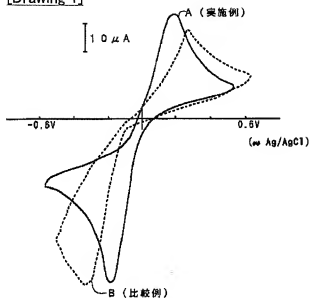
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

---

DRAWINGS

---

[Drawing 1]



---

[Translation done.]



(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平9-265989

(43) 公開日 平成9年(1997)10月7日

(51) Int. Cl. <sup>4</sup>	類別記号	片内整理番号	P I	技術表示箇所
H 0 1 M 4/90			H 0 1 M 4/90	
4/02			4/02	B
10/90			10/90	Z

特許請求 未請求 特許項の数 6 O L (全 4 頁)

(21) 出願番号	特願平8-72596	(71) 出願人	000005805 矢崎電業株式会社 東京都港区三田1丁目4番28号
(22) 出願日	平成8年(1996)3月27日	(72) 発明者	直井 豊彦 東京都小金井市貫井町2-10-2
		(72) 発明者	島健 昭彦 静岡県裾野市御宿1500 矢崎電業株式会社 内
		(72) 発明者	飯塚 弘 静岡県裾野市御宿1500 矢崎電業株式会社 内
		(74) 代理人	弁理士 西野 秀雄 (外1名)

(54) 【発明の名称】 電極材料及び二次電池

(57) 【要約】

【課題】 本発明は、二次電池の電極材料に応用した場合に、室温でも大電流による充放電が可能なスルフィド系電極材料、及び室温での大電流による充放電が可能な二次電池を提供する。

【解決手段】 テオケトン基を有するスルフィド系電極材料。

(2)

特開平9-265989

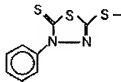
1

【特許請求の範囲】

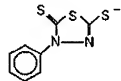
【請求項1】 チオケトン基を有することを特徴とするスルフィド系電極材料。

【請求項2】 化1に示される基または/及び化2に示されるイオンを有することを特徴とする請求項1に記載のスルフィド系電極材料。

【化1】



【化2】



【請求項3】 5, 5'-ジチオビス(3-フェニル-1, 3, 4-チアジアゾール-2-チオン)を含有することを特徴とする請求項1に記載のスルフィド系電極材料。

【請求項4】 チオケトン基を有する物質を含有することを特徴とする二次電池。

【請求項5】 化1に示される基または/及び化2に示されるイオンを有する化合物を含有することを特徴とする請求項4に記載の二次電池。

【請求項6】 5, 5'-ジチオビス(3-フェニル-1, 3, 4-チアジアゾール-2-チオン)を含有することを特徴とする請求項5に記載の二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、電池用電極材料に関する。更に詳しくは、スルフィド系電極材料に関するものである。

【0002】

【従来の技術】近年、通信機器やOA機器の小型化がすすみ、これら機器の軽量化及び小型化競争が繰り広げられている。このような各種機器や、或いは電気自動車等の電源として利用される二次電池においてもその高効率化が求められている。この要求に対し、新たな電極材を用いた電池が開発されつつあるが、この中でエネルギー密度が比較的高いことから、スルフィド化合物を用いた電極材料（以下「スルフィド系電極材料」と言う）

（米国特許第483048号等）が注目されている。このものは、トリアジン環を有する、或いはチアジアゾール環を有するスルフィド化合物などを電極材料に用いるものである。

2

【0003】ここで、スルフィド化合物をR-S-S-R（Rは有機官能基）と表したとき、スルフィド結合（S-S結合）は電解還元による2電子の供給により断裂し、電解液中のカチオン或いはプロトン（M<sup>+</sup>）と結合して2（R-S<sup>-</sup>-M<sup>+</sup>）となり、電解開始時には元のR-S-S-Rに戻って、2電子を放出する。この二次電池においては、通常の他の二次電池並の150Wh/kg以上のエネルギー密度が期待できるとされている。しかし、前述の米国特許の発明者らがJ.Electrochem.Soc. Vol.136, No.9, p.2575-2575 (1989) で報告している

内容から、このスルフィド系二次電池の電極反応の電子移動速度は極めて遅く、従って、室温付近では実用に見合う大電流を取り出すことが困難であり、60℃以上での使用に限られると云う問題が指摘された。

【0004】その後、このスルフィド系二次電池を改良し、大電流に対応させる技術として、特開平5-74459号公報等に示されるように、チアジアゾール環及びスルフィド基を有する有機化合物にポリアクリン等の導電性高分子を組み合わせた電極材料が提案された。しかし、このような改良が行われたにも関わらず、やはり室温下において充分な大電流を取り出すことはできなかった。

【0005】

【発明が解決しようとする課題】本発明は、二次電池の電極材料に応用した場合に、室温でも大電流を取り出すことができるスルフィド系電極材料、及び室温でも大電流を取り出すことが可能な二次電池を提供することを目的とする。

【0006】

【課題を解決するための手段】本発明の有機電極材料は、上記課題を解決するために、請求項1に記載の通りチオケトン基を有するスルフィド系電極材料である。

【0007】

【発明の実施の形態】本発明においてスルフィド系電極材料とは、電解還元によりS-S結合を形成する、或いは/及び、電解還元によりS-S結合が断裂する反応に関与する硫黄原子を有するものを指す。なお、ここでS-S結合とは、2個の硫黄原子によって形成されるスルフィド結合であっても、S-S-S等で示される3個以上の硫黄原子が連続して結合したいわゆるポリスルフィド結合であってもよい。

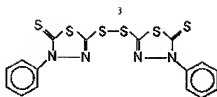
【0008】なお、化1に示される基、或いは化2に示されるイオンを有する物質の場合、フェニル基の影響により、S-S結合の生成・断裂反応に対する促進効果が著しいので好ましい。特に、二重体である5, 5'-ジチオビス(3-フェニル-1, 3, 4-チアジアゾール-2-チオン)（化3参照）であると、充放電サイクルが多くなった際にもその容量の減少が極めて少ないので望ましい。

【化3】

50

(3)

特開平9-265989



【0009】しかし、化1に示される基及び化2に示されるイオンにおいて、3位の置換基がS-S結合の生成・解離反応に対する影響が大きく、そのためこれらのようにフェニル基であることが望ましい。しかし、フェニル基の代わりに、エチル基等のアルキル基、アミノ基、カルボキシル基、アルキルアミノ基、アミド基或いは水素を導入したのもを用いる。また、フェニル基の代わりにチオール基を有するものである場合、チアジアゾールチオンのジスルフィドポリマーを形成する。また、化1における3位の置換原子は、炭素原子その他と置換されていてもよい。

【0010】なお、上記物質は導電性を有しないため、電子導電材、イオン導電材と併用し正極を作製する。電子導電材としては、カーボン或いはチタン、ニッケル等の金属粉などを用いることができ、また、イオン導電材としては過塩素酸塩等の電解質塩とプロピレンカーボネート、エチレンカーボネート、1,2-ジメトキシエタン、1,2-ジエトキシエタン、γ-ブチロラクトン、テトラヒドロフラン、2-メチルテトラヒドロフラン、1,3-ジオキソラン、4-メチル-1,3-ジオキソラン、ジエチルエーテル、スルホラン、アセトニトリル、プロピオニトリル、アニソール等の溶媒とを混合した液体電解質、或いは電解質塩を溶解させたポリエチレンオキサイド等の固体電解質が挙げられる。このような液体電解質、高分子固体電解質のいずれも、電池の電解質として用いることができるが、固体電解質を用いた場合、正極と負極との接触を防止するセパレータの役割も同時に果たすので望ましい。

【0011】また、電解質としては、例えばリチウム二次電池の場合、 $\text{LiPF}_6$ 、 $\text{LiClO}_4$ 、 $\text{LiAsF}_6$ 、 $\text{LiBF}_4$ 、 $\text{LiCF}_3\text{SO}_3$ 等が使用可能である。これらは、適切な濃度になるよう上記有機溶媒に溶解されて電解液を形成する。陰極としては、通常二次電池に用いられている電極を用いることができる。例えばリチウム二次電池の場合、金属リチウム、リチウム-アルミニウム合金、或いはリチウムと黒鉛や炭素などの層間化合物などが挙げられる。これら正極、電解液及び陰極を組み合わせて電池を形成するが、そのときの電池形状、すなわち薄型電池、円筒型或いは角形などを開わず応用することが可能である。

【0012】

【実施例】

【5,5'-ジチオビス(3-フェニル-1,3,4-チアジアゾール-2-チオン)の合成】アルゴン雰囲気

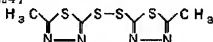
(3)

4

下で、30mlのメタノールに5mmolのヨウ素を溶解し、これに予め5-メルカプト-3-フェニル-1,3,4-チアジアゾール-2-チオンのカリウム塩(ヒドラス化学より入手)10mmolを30mlのメタノールに溶解した溶液をゆっくり滴下し、その後、3時間攪拌し、次いで-40℃に冷却し、生じた沈殿物を濾過によって分離した後沈殿物をメタノールで洗浄し、これを減圧乾燥後、エタノールによって3回再結晶を行って、5,5'-ジチオビス(3-フェニル-1,3,4-チアジアゾール-2-チオン)(化3参照)を得た。

【0013】【2,2'-ジチオビス(5-メチル-1,3,4-チアジアゾール)の合成】アルゴン雰囲気下で、30mlのメタノールに5mmolのヨウ素を溶解し、これに予め2-メルカプト-5-メチル-1,3,4-チアジアゾール10mmol、ナトリウムメトキシ5mmolを30mlのメタノールに溶解した溶液をゆっくり滴下し、その後、3時間攪拌し、次いで-60℃に冷却し、生じた沈殿物を濾過によって分離し、減圧乾燥後、エタノールによって3回再結晶を行って、2,2'-ジチオビス(5-メチル-1,3,4-チアジアゾール)(化4参照)を得た。

【化4】



【0014】これら得られた生成物については、FAB質量分析器、赤外分光分析装置によって目的物であることが確認されている。

【0015】上述のようを得た5,5'-ジチオビス(3-フェニル-1,3,4-チアジアゾール-2-チオン)、及び、2,2'-ジチオビス(5-メチル-1,3,4-チアジアゾール)を用いて電池を形成した。なお、以下の作業はすべてグローブボックス内アルゴン気流で行った。

【0016】電解質としてトリフルオロメタンスルホン酸リチウム( $\text{LiCF}_3\text{SO}_3$ )を0.2mmol/lの濃度になるよう30mlのγ-ブチロラクトンに溶解した電解液を2つ調製し、これらそれぞれに上記で合成した5,5'-ジチオビス(3-フェニル-1,3,4-チアジアゾール-2-チオン)と、2,2'-ジチオビス(5-メチル-1,3,4-チアジアゾール)の2つのジスルフィド化合物を5mmol/lの濃度になるよう溶解した。

【0017】これらの2種の溶液を用いて、それぞれ試料極としてグラフィーカーボン、対極として白金網、参照極として銀/塩化銀電極を用いて電池を形成した。このとき5,5'-ジチオビス(3-フェニル-1,3,4-チアジアゾール-2-チオン)を有する電池を電池A(実施例)、2,2'-ジチオビス(5-メチル-1,3,4-チアジアゾール)を有する電池を電池B

(4)

特開平9-265989

5

6

(比較例)とした。これら電池A及びBについて23℃において走査速度を50mV/秒としてサイクリックボルタモグラムを測定した。これら結果を共に図1に示す。

【0018】これら電池A及び電池Bのサイクリックボルタモグラムを比較すると、酸化電流のピークを示す酸化電位と還元電流のピークを示す還元電位のずれは電池Aでは340mVであり、電池Bでは520mVであって、電池Aにおけるずれは電池Bにおけるずれより小さい。したがって電極反応論によれば、本発明に係る5、5'-ジチオビス(3-フェニル-1,3,4-チアジアゾール-2-チオン)を有する電池Aは、従来用いら

れてきた2,2'-ジチオビス(5-メチル-1,3,4-チアジアゾール)を有する電池Bに比べ、室温における大電流での充放電に適していることが判る。

【0019】

【発明の効果】本発明に係る電極材料を用いて作製した二次電池は、従来のチアジアゾール環を有するスルフィド系電極材料を用いた二次電池に比較すると室温でも大電流を取り出すことが可能である。

【図面の簡単な説明】

【図1】本発明の実施例である電池A及び比較例である電池Bのサイクリックボルタモグラムである。

【図1】

